Mechanism for sludge acidification in aerobic treatment of coking wastewater

Yu-Mei Chao [a], I.-Cheng Tseng [b], Jo-Shu Chang [c],*

[a] *Chemical Process & Water Treatment Section, Division of New Materials R&D, China Steel Corporation, Kaohsiung, Taiwan*
[b] *Department of Biology, National Cheng Kung University, Tainan, Taiwan*
[c] *Department of Chemical Engineering, National Cheng Kung University, No. 1 University Road, Tainan 701, Taiwan*

Abstract

This work was undertaken to investigate the cause of sludge acidification that led to disruption of the activated sludge process treating coking wastewater from a steel-making plant in Taiwan. An activated sludge reactor (ASR) with a working volume of 80 L was used as a model system to simulate the behavior of the real wastewater treatment process. Parameters that may cause acidification or inactivation of the sludge (NH_3, SCN^-, $S_2O_3{}^{2-}$ and CN^-) were studied individually to examine for their effects on the performance of the ASR. The results show that high loading of NH_3, SCN^- and CN^- did not lead to pH decrease, while the ASR attained 85% COD removal and nearly 100% SCN degradation. In contrast, when the wastewater was supplemented with ca. 1000 mg/L of $S_2O_3{}^{2-}$, the pH dropped to nearly 4.0 in 2 days and the COD and SCN removal yields were significantly lower (at 50 and 0–20%, respectively). Thus, overloading of $S_2O_3{}^{2-}$ was apparently a key factor causing sludge acidification. The results suggest that to ensure a normal functioning of the activated sludge, the influent $S_2O_3{}^{2-}$ concentration should be closely monitored and that the pH control of the ASR is indispensable when the $S_2O_3{}^{2-}$ loading is in excess.
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1. Introduction

Phenolic and cyanide (CN^-) compounds are often produced from coking processes. The cyanides are further converted to thiocyanate (SCN^-) via chemical means to reduce its toxicity [1]. Meanwhile, thiosulphate ($S_2O_3{}^{2-}$) was usually formed due to oxidation of hydrogen sulphide (H_2S) and/or sulphur (S^o). The biological treatment of coking wastewater has been successfully developed, but there have still been cases of process instability and inhibition leading to inconsistent or poor performance of the treatment plant [2,3]. China Steel Corporation (CSC) has over 20 years' experience in treating the coking wastewater from coal processing plants. Normally 85% COD removal and nearly complete degradation of thiocyanate and cyanides have been attained via an activated sludge process with an aeration chamber of 7350 m^3 and a total hydraulic loading of 6000–7500 m^3/days.

However, in the past few years, the biological treatment plant has functioned abnormally about 3–4 times a year. In those cases, the effluent COD increased to 500–1000 mg/L (effluent COD was 200–300 mg/L under normal operation) and SCN^- was barely removed. In addition, the sludge settling became inefficient and the pH of the sludge dropped to nearly 4.0, despite the pH in the influent being adjusted to 7.0–7.5 constantly. It usually took 2–6 weeks for the activated sludge system to return to its normal performance, thus causing a severe problem in maintaining the quality of wastewater treatment.

Efforts have been made to investigate the effects of hydraulic retention time (HRT = 14–24 h) and dissolve oxygen level (0.5 to over 2.0 mg/L) on the performance of the activated sludge process. It was found that both factors had limited effects on the treatment efficiency and did not cause the decrease in pH. However, sludge acidification seems to be the major problem leading to disruption of the biological treatment process. Thus, there is an urgent demand to identify the cause of sludge acidification and find a feasible resolution to the problem of process instability.

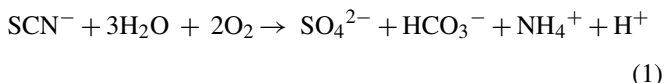
Table 1
Characteristics of coking wastewater from a steel-making plant of China Steel Corporation

Parameter	Characteristics
Hydraulic loading (m^3/days)	6000–7500
COD (mg/L)	1800–2300
pH	6.5–7.5
CN$^-$ (mg/L)	<15
SCN$^-$ (mg/L)	250–400
S$_2$O$_3{}^{2-}$ (mg/L)	200–250
T–NH$_3$–N (mg/L)	500–800
T-phenol (mg/L)	250–300
S^0, S^{2-}	nd
SO$_4{}^{2-}$ (mg/L)	300–1000

nd: not detected.

According to the composition of the coking wastewater as well as microbiological and biochemical principles, possible routes of acidification in the activated sludge include thiocyanate degradation (Eq. (1)), oxidation of thiosulphate (Eq. (2)), nitrification of ammonia (Eqs. (3) and (4)), and biotic oxidation of pyrite (FeS$_2$) or elementary sulphur (S^o) [4,5]. Since the content of FeS$_2$ and S^o was negligible in the coking wastewater (Table 1), the former three routes were investigated for their possibility to cause sludge acidification.
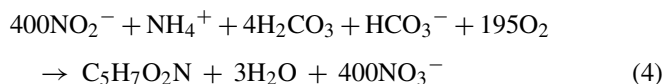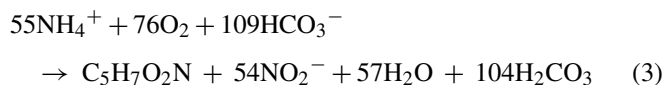
Thiocyanate degradation [3]

$$SCN^- + 3H_2O + 2O_2 \rightarrow SO_4{}^{2-} + HCO_3{}^- + NH_4{}^+ + H^+ \tag{1}$$

Thiosulphate oxidation [6]

$$S_2O_3{}^{2-} + 2O_2 + H_2O \rightarrow 2SO_4{}^{2-} + 2H^+ \tag{2}$$

Ammonia nitrification

$$55NH_4{}^+ + 76O_2 + 109HCO_3{}^- \rightarrow C_5H_7O_2N + 54NO_2{}^- + 57H_2O + 104H_2CO_3 \tag{3}$$

$$400NO_2{}^- + NH_4{}^+ + 4H_2CO_3 + HCO_3{}^- + 195O_2 \rightarrow C_5H_7O_2N + 3H_2O + 400NO_3{}^- \tag{4}$$

In this study, an 80 L model activated sludge reactor was loaded with a high concentration of the suspected components (NH$_3$, SCN$^-$, S$_2$O$_3{}^{2-}$) that might cause acidification. In addition, the toxic effect of toxic cyanide was also studied. The purpose was to provide a more complete understanding of the process biochemistry to help the plant maintain a stable and efficient operation, especially when sludge acidification occurs.

2. Materials and methods

2.1. Characteristics of the wastewater and activated sludge

The influent used in this study is the real coking wastewater, mainly containing phenolic compounds (T-phenol), ammonia
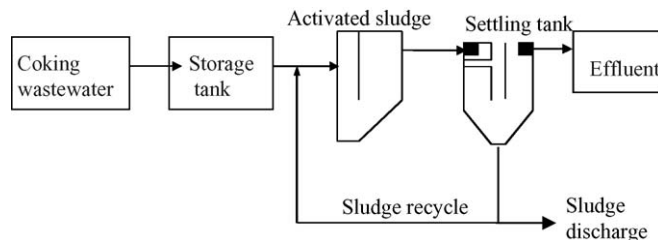

Fig. 1. A schematic description of the model activated sludge reactor (ASR).

(T–NH$_3$–N), SCN$^-$, CN$^-$, S$_2$O$_3{}^{2-}$, SO$_4{}^{2-}$, etc. Typical composition of the coking wastewater is shown in Table 1. The pH of the wastewater was adjusted to 7.0–7.5 in a buffer tank by addition of NaOH before entering the activated sludge reactor. The chemical oxygen demand (COD) of the influent was within the range of 1800–2300 mg/L. Typical MLSS concentration of the activated sludge was 5000 mg/L and the dissolved oxygen (DO) level was normally higher than 2 mg/L. The industrial activated sludge process that used to treat coking wastewater of CSC was carried out with a hydraulic retention time (HRT) of 24 h and a sludge retention time (SRT) of approximately 30 days.

2.2. Setup of the model activated sludge reactor

The schematic description of the activated sludge reactor (ASR) used in this study is shown in Fig. 1. The main body of the ASR consisted of a 80 L aeration chamber connected with a sedimentation unit (30 L), where part of the settled sludge was recycled to allow a SRT of 30 days (identical to the industrial process). The wastewater was evenly mixed and adjusted to pH 7.5 in a 1000 L storage tank prior to being fed into the aeration chamber for biodegradation.

2.3. Operation of activated sludge reactor with possible inhibitors

At start-up, the reactor was first seeded with effluent activated sludge collected from secondary treatment plant of CSC, and then fed with the coking wastewater (Table 1) at HRT = 24 h, which is identical to the industrial activated sludge process. After stable operation was achieved, the feed (in the storage tank) was loaded with possible inhibitors, including NH$_3$, SCN$^-$, and S$_2$O$_3{}^{2-}$ (ca. 1000 mg/L each) or CN$^-$ (25–60 mg/L). The composition and pH of both the influent and effluent were monitored with respect to time to observe their effects on the performance of the activated sludge.

2.4. Operation of ASR with pH control

Coking wastewater loaded with 1000 mg/L of S$_2$O$_3{}^{2-}$ was fed into two identical model activated sludge reactors. In one set, the pH in the system was controlled at 6.0–7.0 by automatic NaOH titration, while in the other set the pH was not controlled. The composition and pH of influent and effluent were monitored with respect to time.

2.5. Strain isolation and identification

Samples taken from activated sludge treating CSC coking wastewater were pre-cultured and then grown on selective medium containing phenol, SCN^-, and $S_2O_3^{2-}$, respectively, as the sole carbon source. The colonies grown on the selective plates were purified and the genomic DNA of each isolate was extracted for amplification and sequence analysis of the 16S rRNA gene. The sequence was then compared with others available in NCBI GenBank for identification.

2.6. Analytical methods

The concentration of SCN^- and $S_2O_3^{2-}$ in the wastewater was determined by ion chromatography (Dionex, model DX-120) using an AS-11 column. SO_4^{2-} and NO_3^- were also detected by ion chromatography (Metrohm, model 732). Concentrations of total ammonia nitrogen, phenolic compounds, COD, and alkalinity were determined by standard methods [7].

DO level was analyzed by a DO meter (WTW; model Oxi 315i, Germany).

3. Results and discussion

3.1. Effect of high NH_4^+ and CN^- loading

The influent was amended by high concentration of NH_3 (ca. 1200 mg/L) or CN^- (25–60 mg/L) to examine if nitrification causes acidification of wastewater and if a high CN^- concentration affects the performance of activated sludge. Fig. 2 show that the increasing loading of influent NH_3 did not affect the efficiency of COD and SCN^- removal, which was maintained at 85 and 100%, respectively, during 14 days of operation. Moreover, the increase in NH_3 did not trigger nitrification as the nitrate concentration in the effluent was still very low. Instead, the NH_3 concentration in the effluent was slightly higher than that in the feed because degradation of SCN^- produced NH_3 (Eq. (1)). The pH value in the system remained fairly stable at approximately 5.6–6.0. Therefore, a sharp increase in NH_3 loading is not a major cause for acidification resulting in reactor anomalies.
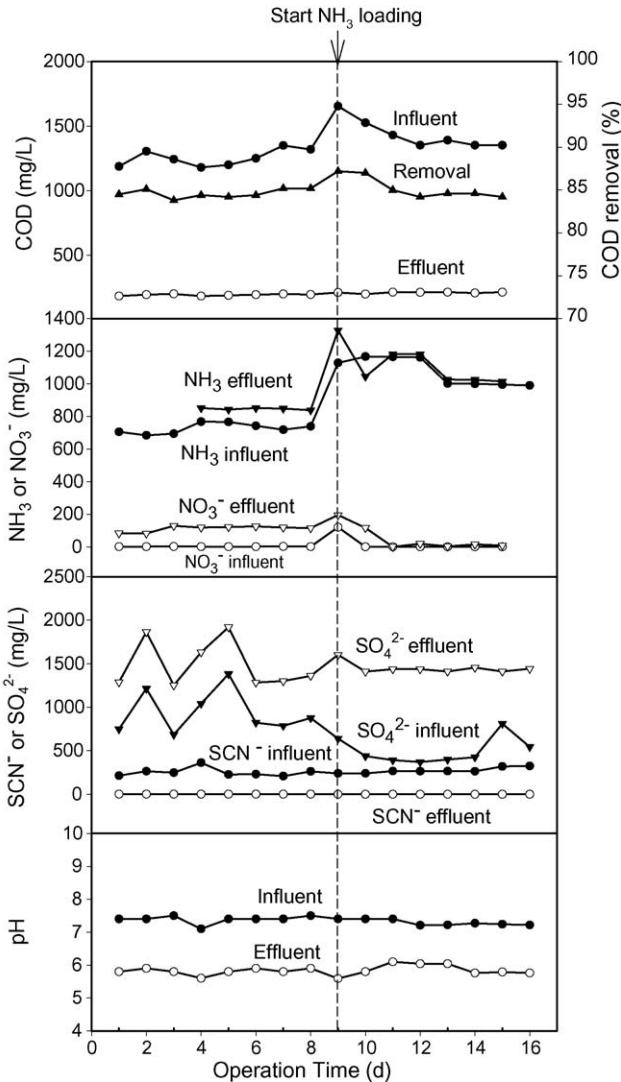

Fig. 2. Chemical composition and pH in the influent and effluent of NH_3-loaded activated sludge reactor.
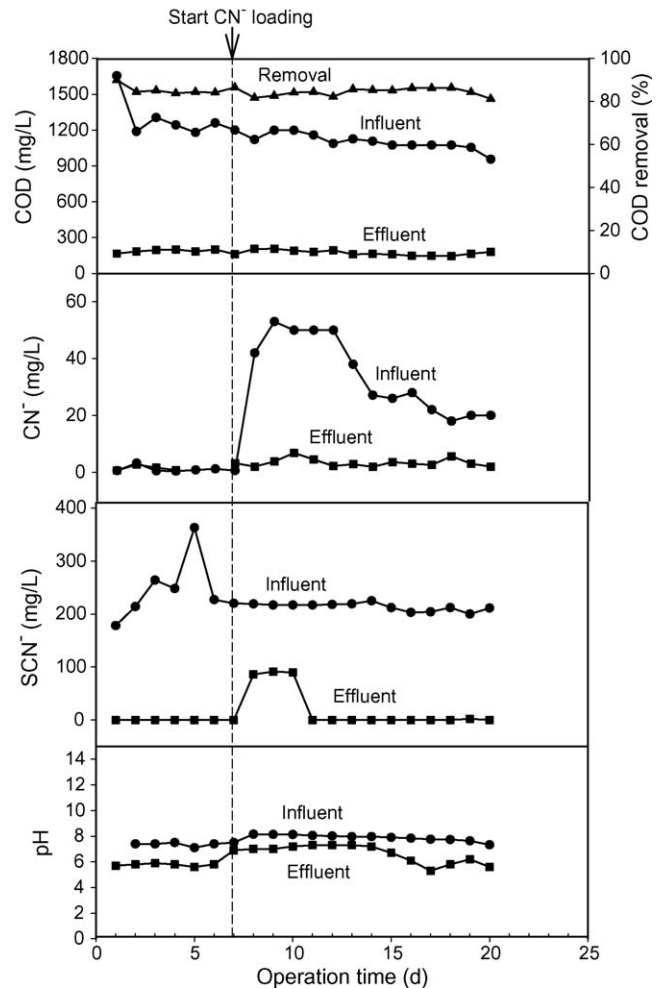

Fig. 3. Chemical composition and pH in the influent and effluent of CN^--loaded activated sludge reactor.

In contrast to the negligible effect by high ammonia loading, a sudden increase in CN^- concentration (25–60 mg/L) caused a less efficient degradation of COD and SCN^- during the first 2 days after CN^- loading. The removal efficiency of COD and SCN^- dropped to 80 and 55%, respectively (Fig. 3), indicating a slight toxic effect of cyanide. However, the system was soon recovered after 3 days and the removal of COD and SCN^- increased to 85 and 100%, respectively. The ASR displayed an efficient CN^- degradation as the concentration of CN^- in the effluent was always below 5 mg/L (Fig. 3). The addition of CN^- to the feed did not alter the pH, which remained at 5.5–6.5 throughout the experiments.
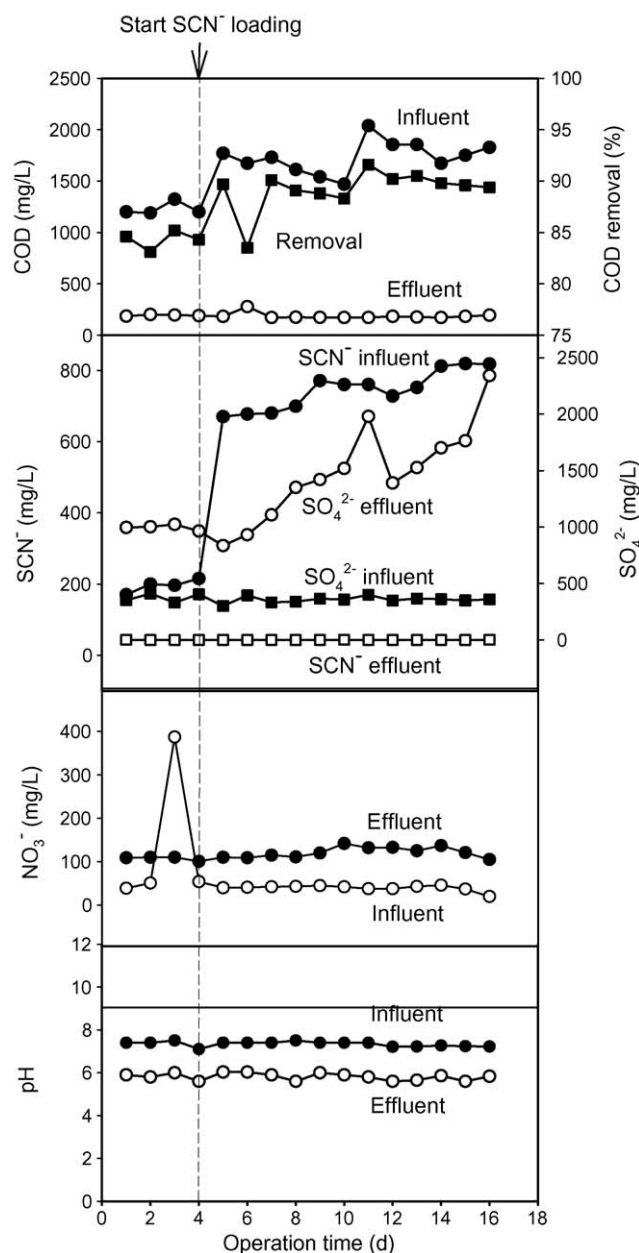
3.2. Effect of high SCN^- loading

The coking wastewater usually contains a significant amount of SCN^- [1], which can be oxidized aerobically by thiocyanate-degrading bacteria to produce sulphuric acid (Eq. (1)) [3]. Thus, SCN^- is highly suspected to cause sludge acidification. Effect of high SCN^- loading on the performance of ASR is demonstrated in Fig. 4. It can be observed from Fig. 4 that a large amount of SO_4^{2-} evolved along with a higher SCN^- loading (700–900 mg/L) due to the reaction indicated in Eq. (1), showing that SO_4^{2-} is produced during degradation of SCN^-. Removal of COD and SCN^- was effective with a depletion yield of 85 and 100%, respectively. Nitrification was not provoked regardless of formation of ammonia arising from oxidation of thiocyanate (Eq. (1)), since the nitrate concentration in the effluent was always below 50 mg/L. Although acid was produced during oxidation of SCN^-, the pH in the reactor was essentially maintained at a level of 5.5–6.0 (Fig. 4). This may be attributed to
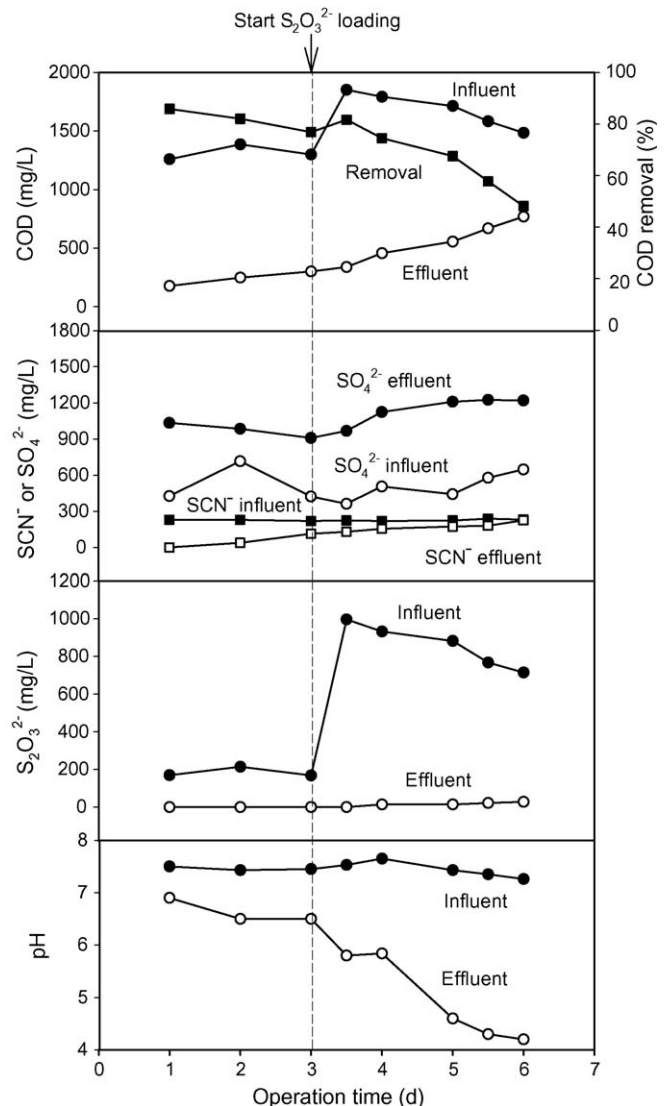

Fig. 4. Chemical composition and pH in the influent and effluent of SCN^--loaded activated sludge reactor.

Fig. 5. Chemical composition and pH in the influent and effluent of $S_2O_3^{2-}$-loaded activated sludge reactor.

Table 2
Documented and identified bacterial populations and functions in the activated sludge treating coking wastewater in China Steel Corporation (CSC)

Function	Suitable pH for growth [1,6,8–11]	Strains isolated[a] or documented [1,6,8–11]	
Degradation of phenolic compounds	5.0–9.0	*Acinetobacter* sp.[a]	*Oceanimons baumannii*
		Arthrobacter sp.	*Pseudomonas aeruginosa*
		Bacillus sp.[a]	*Pseudomonas putida*
		Bacillus sp.[a]	*Rhodococcus rhodochrous*
		Citrobacter braakii	*Spiroplasma floricola*
		Microbacterium sp.	*Staphylococcus aureus*
		Mycoplasma spermatophilum	*Vibrio cyclosites*
Degradation of thiocyanate	6.0–9.0	*Acinetobacter* sp.	*Thiobacillus thioparus*[a]
		Paracoccus thiocyanatus	*Thiobacillus* sp.[a]
		Methylobacterium thiocyanatum	
Thiosulphate oxidation	6.0–9.0	*Thiobacillus thioparus*[a]	*Thiobacillus* sp.[a]
	1.3–4.5	*Thiobacillus denitrificans*[a]	*Thiobacillus ferrooxidans*
		Thiobacillus acidophilus[a]	

[a] Bacterial strains isolated from the CSC activated sludge and identified via 16S rDNA sequence matching.

the simultaneous formation of basic products, such as HCO_3^- and NH_4^+ during degradation of SCN^- (Eq. (1)). The resulting alkalinity in the ASR seemed to be able to neutralize the acidic products generated from degradation of high concentration of thiocyanate. It is worth noting that the SCN^- degraders are usually unable to grow in acidic conditions (pH < 6.0) [1,6], which may also regulate acid production rate from of thiocyanate degradation.

3.3. Effect of high $S_2O_3^{2-}$ loading

Another possible mechanism of sludge acidification is the oxidation of reduced sulphuric compounds, such as thiosulphate, which is present in coking wastewater at a typical concentration of 200–250 mg/L. The reaction for biotic oxidation of thiosul-phate is shown in Eq. (2). After addition of ca. 1000 mg/L of $S_2O_3^{2-}$ in the feed for 10 h, the pH of activated sludge started to decrease, and the pH dropped rapidly from 6.0 to 4.0 after 2 days of $S_2O_3^{2-}$ loading (Fig. 5). The degradation of COD and SCN^- also decreased in this period. After being operated at high $S_2O_3^{2-}$ loading for 3 days, the sludge degraded only 45% of influent COD, while SCN^- was barely decomposed. In contrast, conversion of $S_2O_3^{2-}$ was above 90% during the entire operation, accompanied by an evolution of SO_4^{2-} possibly following Eq. (2) (Fig. 5). This indicates that at low pH, the thiosulphate-degrading bacteria were still active. This is supported by the isolation of two types of acidophilic $S_2O_3^{2-}$ degraders from the activated sludge (Table 2). Moreover, bulking of the acidified sludge occurred (Fig. 6A) and fungal species were observed from the sludge sample (Fig. 6B), probably due to the severe
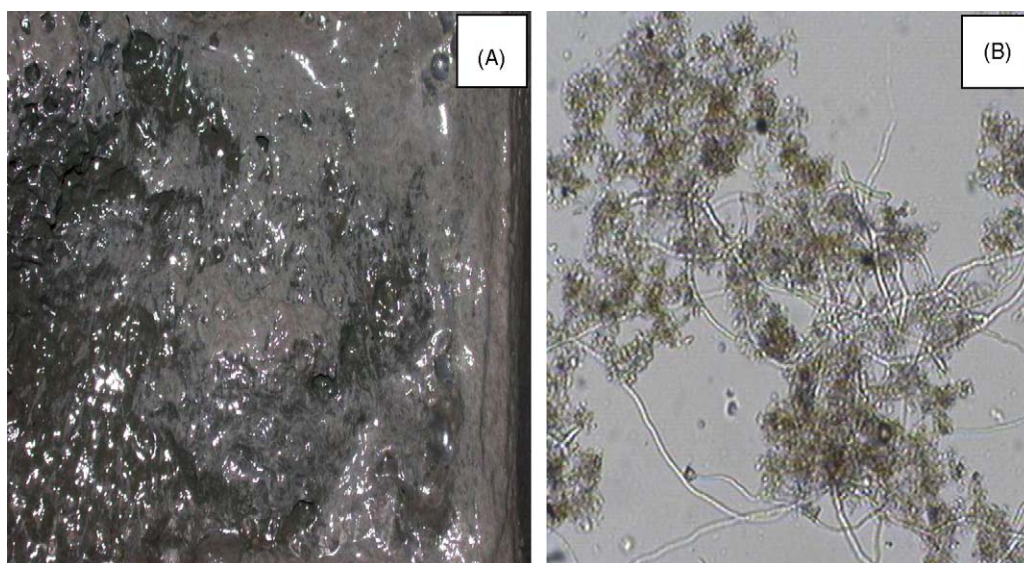

Fig. 6. Sludge from high $S_2O_3^{2-}$ loading simulative ASR. (A) Sludge bulking in the ASR and (B) sludge image under light microscope (OLYMPUS Model BH2; Tokyo, Japan).

acidic condition. These results suggest that the main reason for sludge acidification during the treatment of coking wastewater was an abnormal high loading of $S_2O_3^{2-}$. Since oxidation of 1 mol $S_2O_3^{2-}$ produced 2 mol of H^+ (Eq. (2)), the added $S_2O_3^{2-}$ (800–1000 mg/L) seemed to exceed the reactor's buffer capacity of alkalinity, leading to a decrease in pH. Measurement of the alkalinity in the $S_2O_3^{2-}$-loaded influent (at pH 7.4) shows that the residual alkalinity in the effluent was less than 5 mg/L when the $S_2O_3^{2-}$ concentration was 250 mg/L. Therefore, acidification may sensitively occur when $S_2O_3^{2-}$ loading is higher than 250 mg/L. In comparison, biotic oxidation of 1 mol SCN^- produces 1 mol of H^+, but 1 mol of HCO_3^- and NH_4^+ is also formed (Eq. (1)) alleviating the acidic effect.

3.4. Influence of acidification on bacterial community in activated sludge reactor

According to chemical composition of the coking wastewater, three major groups of bacterial populations may be present in the activated sludge system, including microorganisms that utilize phenolics, thiocyanate, or thiosulphate as the substrate. Table 2 lists the strains possessing the ability of degrading the aforementioned substrates as well as the favorable pH ranges for their growth [1,6,8–11]. Pure strains were also isolated from the activated sludge and the identified bacterial isolates are marked in Table 2. Inspection of the pH range for cell growth shows that a low pH (below 5.0) appears to inhibit the growth of strains responsible for degradation of phenolics and thiocyanate, whereas the acidic condition seems to be favorable for the growth of some thiosulphate-oxidizing bacteria (e.g., *Thiobacillus denitrificans* and *Thiobacillus acidophilus*) (Table 2). This observation is consistent with the results indicated in Fig. 5, showing that the removal yields of phenolics (essentially represented by COD) and thiocyanate markedly decreased when sludge was acidified to a low pH of 4.0, at which the acidophilic thiosulphate-oxidizing bacteria may become dominant.

3.5. Effect of pH control for ASR under $S_2O_3^{2-}$-enriched feeding

Since sludge acidification reduced biodegradation activity of the system, it is of interest to know if the acidification and the resulting poor treatment efficiency can be prevented by pH control. Hence, the activated sludge reactor, fed with $S_2O_3^{2-}$ (1000 mg/L)-enriched coking wastewater, was operated under a controlled pH ranging from 6.0 to 7.0 using NaOH for instantaneous pH adjustment. A parallel experiment without any pH control was also conducted for comparison. The results show that when the pH was well controlled, the reactor reached steady-state after a short period of operation (3 days) with a COD removal yield of ca. 80–85% and nearly complete degradation of $S_2O_3^{2-}$ and SCN^-. This operation remained fairly stable for 16 days, despite keeping a high $S_2O_3^{2-}$ level in the influent. For the reactor without pH control, acidification took place in 3 days and inefficient treatment for COD (50% removal) and SCN (0–20% removal) was observed. This shows that pH control was effective in preventing the acidification effect originated from $S_2O_3^{2-}$.

3.6. Practical applications

The above finding is of great help to keep our activated sludge system stable. We used to ignore the effect of thiosulphate and did not even monitor the influent $S_2O_3^{2-}$ concentration in the past. The results of this work highlights the significance of the $S_2O_3^{2-}$ content in the feed as well as the effectiveness of pH control. Since early 2003, we have closely monitored the thiosulphate concentration in the coking wastewater and controlled its pH in routine practice. It was found that thiosulphate concentration was essentially within 200–250 mg/L. But in some cases, it abnormally increased to 700–800 mg/L, which might have caused acidification if the pH had not been carefully controlled.

4. Conclusions

This study shows that a shock loading of thiosulphate was most likely the cause of sludge acidification during aerobic treatment of the coking wastewater of China Steel Corporation. Controlling the pH of the activated sludge reactor at 6.0–7.0 was effective in avoiding this adverse effect and in maintaining the biodegradation function. This finding signifies the role of pH control in biological treatment of coking wastewater. At CSC the $S_2O_3^{2-}$ concentration in coking wastewater was occasionally increased to a high value (e.g., 700–800 mg/L) due to improper upstream operations. Through close monitoring, the sludge acidification effect is now avoided by controlling the pH value within a proper range.

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